

RAMAN SPECTROSCOPY
FOR THE FORENSIC EXAMINATION
OF REACTIVELY DYED
COTTON

by

Jane Thomas

A thesis

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degree of Doctor of Philosophy (Science)

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Certificate of Authorship and Originality

I certify that the work in this thesis has not been previously submitted for a degree nor has been submitted as part of the requirements for a degree except as fully acknowledged in the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all the information sources and literature used are indicated in the thesis.

A handwritten signature in dark ink, appearing to read 'Jane Thomas', with a stylized, flowing script.

Jane Thomas

31st October 2005

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List of Abbreviations

| | |
|---------------|--|
| AFP | Australian Federal Police |
| CI | Colour Index |
| CCD | Charged Coupled Device |
| CCTV | Closed Circuit Television |
| DP | Discriminatory Power |
| DNA | Deoxyribose Nucleic Acid |
| EFG | European Fibres Group |
| ENFSI | European Network of Forensic Science Institutes |
| ESI-MS | Electrospray Ionisation – Mass Spectrometry |
| ESI-MS/MS | Electrospray Ionisation – tandem Mass Spectrometry |
| FBI | Federal Bureau of Investigation |
| FPF | Fibre Plastic Fusion |
| FSS | Forensic Science Service |
| FTIR | Fourier Transform Infrared |
| GSR | Gun Shot Residue |
| IR | Infrared |
| MPFSL | Metropolitan Police Forensic Service Laboratory |
| MSP | Microspectrophotometry |
| mW | milli-watt |
| NIR | Near Infrared |
| nm | nano-meter |
| PCA | Principal Components Analysis |
| PCM | Plastic Coating Mark |
| Py-GC | Pyrolysis Gas Chromatography |
| SERRS | Surface Enhanced Resonance Raman Spectroscopy |
| SERS | Surface Enhanced Raman Spectroscopy |
| SWGMAF | Scientific Working Group for Materials |
| TLC | Thin Layer Chromatography |
| TWGFIBE | Technical Working Group for Fiber Examinations |
| UV | Ultraviolet |
| Vis-MSP | Visible Microspectrophotometry |
| XAM | Neutral medium improved white Gurr (Xylene based mountant) |
| ΔE | energy change |
| μm | micro-meter |

Abstract

In the 21st Century, fibre examiners are faced with the constraints of time and money. Rapid advances in DNA technology has seen fibre evidence undervalued due to it being time consuming, costly and (when competing with DNA) perceived to be less discriminatory. However, DNA is not present in all cases and when present may require other evidence to interpret the circumstance/s. The only way forward for fibre examinations is through research that will address issues of time and money whilst increasing their evidentiary value by demonstrating reliability through improved statistical information.

Raman spectroscopy was investigated as it is a technique that is growing in popularity for the analysis of materials. It is quick, discriminatory, non-destructive and requires minimal sample preparation. The ability of Raman spectroscopy to discriminate black/grey and blue cotton fibres was investigated to determine how effective the technique would be for analysing this often undervalued fibre evidence.

Various parameters of Raman spectroscopy were investigated to determine the optimal conditions for the analysis of the samples selected. The major variable investigated was laser wavelength with the 785nm and 632.8nm lasers providing the best results. Results indicated that, at least, the major dye component could be identified using Raman spectroscopy.

The discriminatory power of the technique was then investigated for a sample set of 11 black/grey and blue cotton samples as well as a set of 91 black and blue cotton fibres of unknown dye types. This was then compared to the discriminatory power of microspectrophotometry (MSP) for the same sample sets as well as the discriminatory power of the combined techniques.

In analysis of both sample sets, Raman spectroscopy showed a lower discriminatory power than microspectrophotometry. However, combining the two techniques significantly increased the discriminatory power. Using

chemometrics increased the discrimination provided by Raman spectroscopy indicating that chemometrics may be used as an aid for interpreting data.

Whilst the advantages of Raman spectroscopy were evident during these studies one major limitation of the technique was also highlighted. The problem of fluorescence has long been regarded as the major drawback to using Raman spectroscopy for fibre examinations. The problem was overcome in some instances by changing the laser wavelength but not all.

Even with the occurrence of fluorescence, it was shown that, for the sample sets investigated, Raman spectroscopy (when combined with microspectrophotometry) provided a level of discrimination not able to be achieved with microspectrophotometry as a single technique. Therefore, Raman spectroscopy should be considered when undertaking analysis of these sample types.

Keywords: Fibre evidence, Reactive Dyes, Raman Spectroscopy, Microspectrophotometry, Chemometrics